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⑦① Applicant: DAI-ICHI KOGYO SEIYAKU CO.,
LTD.
55 Nishishichijo Higashikubo-cho
Shimogyo-ku Kyoto(JP)

⑦② Inventor: Tanuchi, Akira
12-6, Daigo Furumichicho, Fushimi-ku
Kyoto(JP)
Inventor: Komori, Hirohito
20-305 Yamanouchi Midodenchō, Ukyo-ku
Kyoto(JP)
Inventor: Niwa, Koichi
11 Katagihara Enomotocho, Nishikiyo-ku
Kyoto(JP)

⑦④ Representative: Strehl, Schübel-Hopf,
Groening
Maximilianstrasse 54 Postfach 22 14 55
D-8000 München 22(DE)

⑤④ Method of producing imide bond-containing resins.

⑤⑦ The invention relates to a method of producing imide bond-containing resins. The method comprises reacting a halogenated phthalic anhydride, a specific copolymer and a diisocyanate compound in an inert solvent in the presence of a quaternary phosphonium compound as a catalyst to give an imide bond-containing resin in high yield. The imide bond-containing resins provide flammable substances with good fire or flame resistance and at the same time themselves have good heat resistance and weather resistance. Therefore, the resins can be used as flame retardants in a broad range of application.

EP 0 401 589 A2

This invention relates to a method of producing imide bond-containing resins.

10 Such flame retardants are required not only to be able to provide plastics with good fire or flame resistance without impairing the intrinsic physical properties of the plastics but also to have, by themselves, good heat resistance and weather resistance.

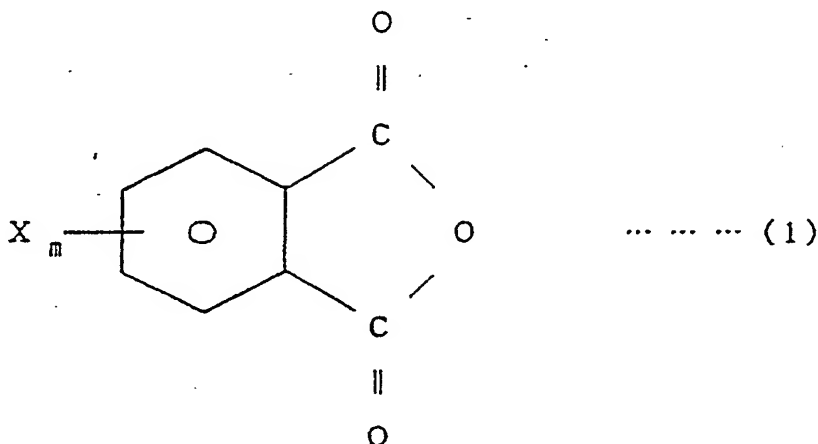
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20 Accordingly, it is an object of the invention to provide a method of producing imide bond-containing resins not only capable of providing plastics with good fire or flame resistance without impairing the physical properties of the plastics but also themselves having good heat resistance and weather resistance.

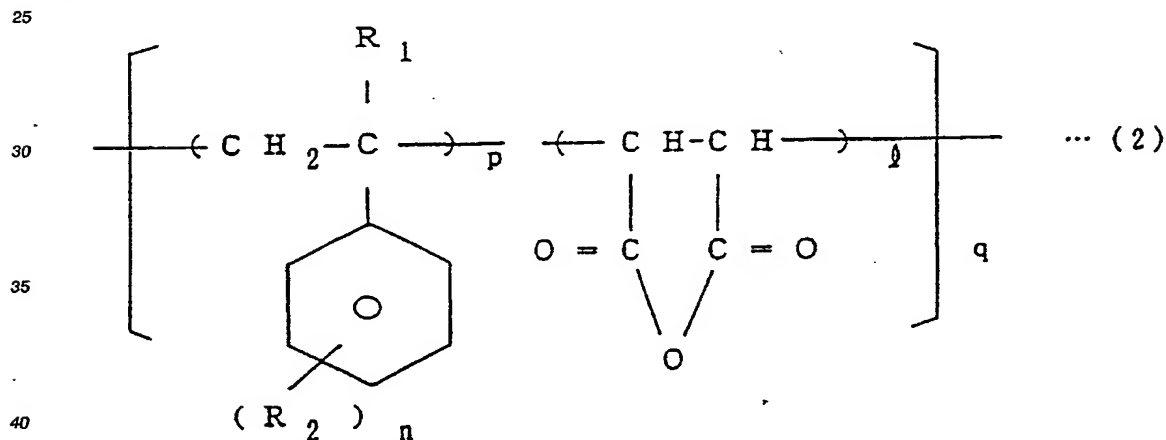
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wherein R_1 is H or CH_3 , R_2 is H, Cl, Br, F or CH_3 , R_3 is an aliphatic, aromatic or alicyclic hydrocarbon group, X is Br, Cl or F, l is equal to 1, m is an integer of 1 to 4, n is an integer of 1 to 5, p is an integer of 1 to 4 and q is a number equal to 1 to 100, which comprises reacting a halogenated phthalic anhydride of the general formula (1)



wherein X and m are as defined above, a copolymer of the general formula (2)



wherein R_1 , R_2 , p , n , l and q are as defined above, and a diisocyanate compound of the general formula (3)

45 $R_3-(\text{NCO})_2$ (3)

wherein R_3 is as defined above, in an inert solvent in the presence of a quaternary phosphonium compound as a catalyst.

DESCRIPTION OF PREFERRED EMBODIMENTS

50 The halogenated phthalic anhydride of general formula (1) to be used in the practice of the invention is, for example, tetrachlorophthalic anhydride, tetrabromophthalic anhydride, dichlorophthalic anhydride or dibromophthalic anhydride.

55 The copolymer of general formula (2) is, for example, a styrene-maleic anhydride copolymer (comonomer mole ratio = 1:1 to 4:1), an α -methylstyrene-maleic anhydride copolymer (comonomer mole ratio = 1:1 to 4:1), a chlorostyrene-maleic anhydride copolymer or a bromostyrene-maleic anhydride

copolymer.

The diisocyanate compound of general formula (3) is, for example, 1,6-hexamethylene diisocyanate, diphenylmethane diisocyanate, tolylene diisocyanate, xylene diisocyanate, isophorone diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated tolylene diisocyanate or hydrogenated xylene diisocyanate.

The quaternary phosphonium compound to be used as a catalyst includes, among others, ethyltriphenylphosphonium chloride, benzyltriphenylphosphonium chloride, phenacetyltriphenylphosphonium chloride, acetonyltriphenylphosphonium chloride, ethyltriphenylphosphonium bromide, butyltriphenylphosphonium bromide, octyltriphenylphosphonium bromide, 2-methylbenzyltriphenylphosphonium bromide, tetraphenylphosphonium bromide, allyltriphenylphosphonium bromide, benzyltriphenylphosphonium iodide and ethyltriphenylphosphonium iodide.

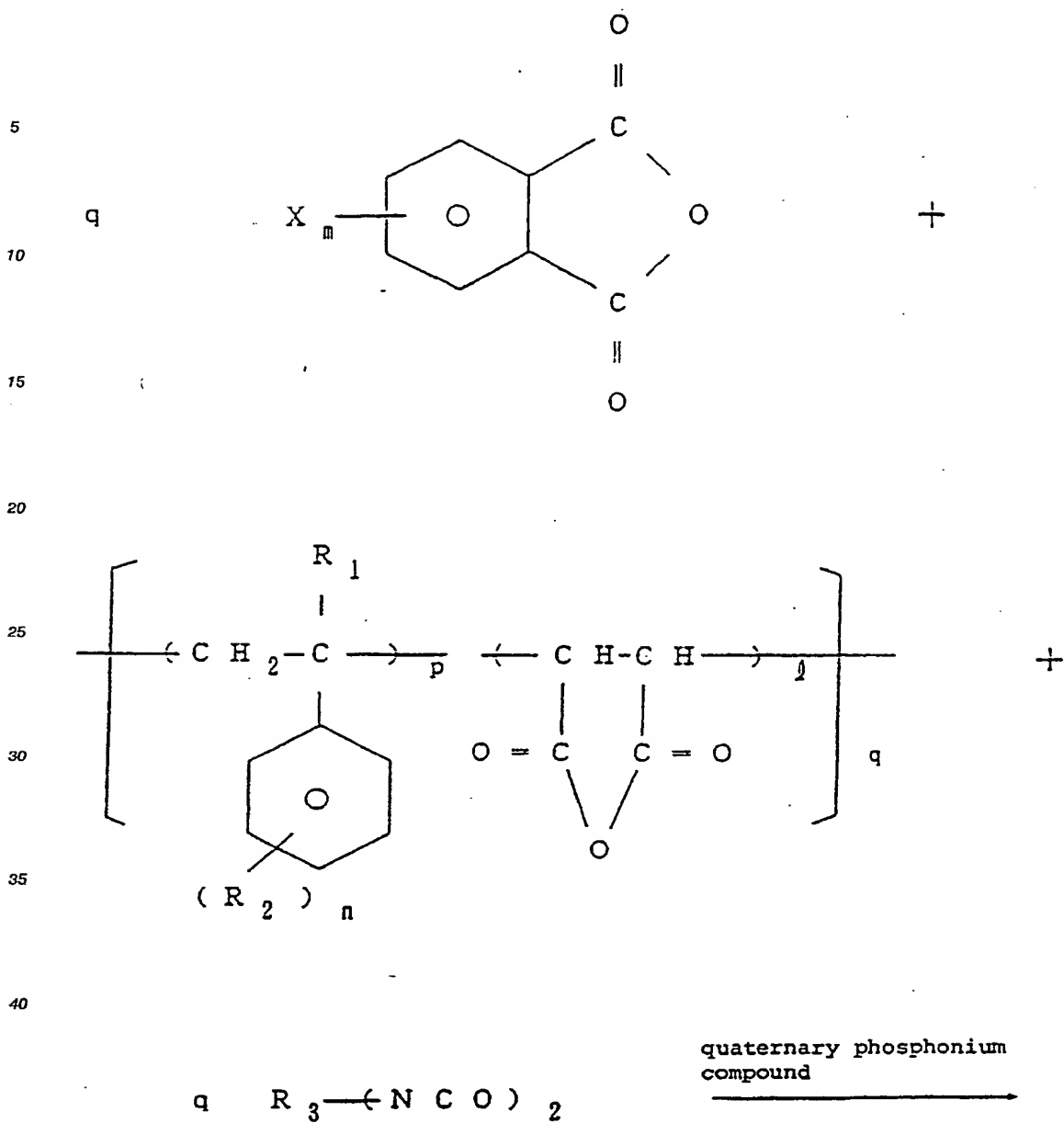
The above-mentioned quaternary phosphonium compound is used preferably in an amount of 0.01-10% by weight of the total amount of halogenated phthalic anhydride of general formula (1) plus copolymer of general formula (2) plus diisocyanate compound of general formula (3).

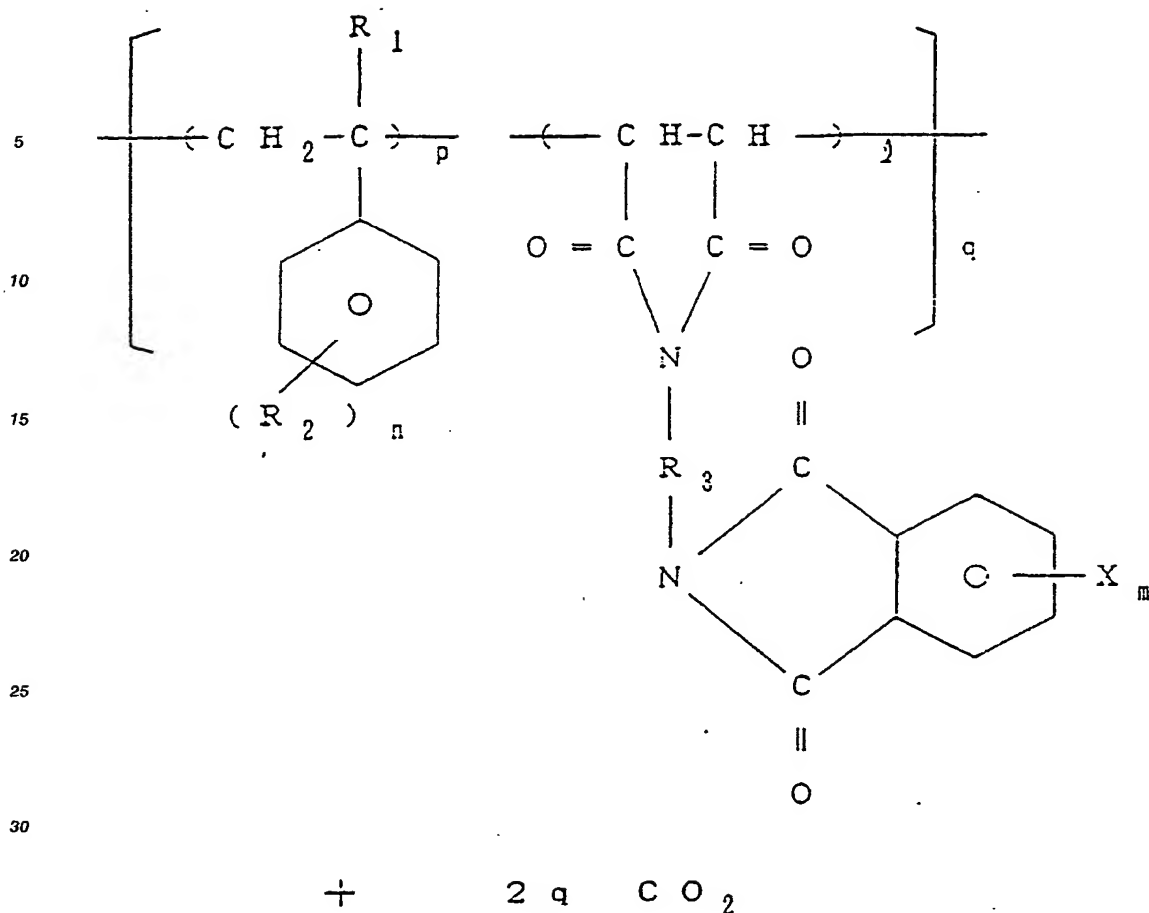
The inert solvent to be used in the practice of the invention is, for example, xylene, toluene, dimethylformamide, dimethylacetamide, benzene, cyclohexane or dimethyl sulfoxide, or a mixture of two or more of such solvents.

The inert solvent is used preferably in an amount of 1 to 10 times the total amount of halogenated phthalic anhydride of general formula (1) plus copolymer of general formula (2) plus diisocyanate compound of general formula (3).

The method of producing imide bond-containing resins of general formula (4) as provided by the present invention consists in reacting the above-mentioned halogenated phthalic anhydride of general formula (1), the above-mentioned copolymer of general formula (2) and the above-mentioned diisocyanate compound of general formula (3) in the inert solvent in the presence of the quaternary phosphonium compound catalyst.

The reaction may be illustrated as follows:





Thus, the above three reactants, namely halogenated phthalic anhydride of general formula (1), copolymer of general formula (2) and diisocyanate compound of general formula (3), each in a stoichiometric amount, are reacted together in the inert solvent in the presence of the quaternary phosphonium compound catalyst. The reaction is complete when the stoichiometric amount of carbon dioxide has been generated. In a specific embodiment, a mixture of the halogenated phthalic anhydride of general formula (1) and the copolymer of general formula (2) is dissolved in the inert solvent and the quaternary phosphonium compound is added thereto. Then, the diisocyanate compound of general formula (3) is added dropwise to the solution with stirring. On this occasion, the temperature is maintained at 60-150° C. After completion of the dropping of the diisocyanate compound of general formula (3), the reaction is allowed to proceed with continued stirring while the reaction system is maintained at 100-150° C. After the diisocyanate compound has been consumed and the reaction product has separated out, the inert solvent is distilled off under reduced pressure, and the reaction product is washed with water and further washed well with 5% aqueous ammonia or an aqueous caustic alkali solution. It is further washed with water and dried to give an imide bond-containing resin representable by the above general formula (4). Alternatively, the reaction product is washed, filtered, washed with an alcohol, e.g. methanol, isopropyl alcohol, etc., acetone, methyl ethyl ketone or the like, filtered again and dried.

The imide bond-containing resin of general formula (4) thus obtained can be used as a flame retardant.

Thus, it can be used as an additive-type flame retardant in general-purpose resins, such as polystyrene resins, polyethylene resins, polypropylene resins, acrylic resins, vinyl chloride resins, saturated or unsaturated polyester resins, melamine resins, epoxy resins and phenol resins, as well as in engineering plastics, such as ABS resins, polyphenylene oxide resins, polycarbonate resins and polyamide resins. It can also be used in the aqueous dispersion form in treating fibers, latices and so forth for providing them with fire or flame resistance.

For use as a flame retardant, it is preferably used in combination with conventional halogen-containing flame retardants and/or phosphorus-containing flame retardants; stabilizers, such as triphenyl-phosphine oxide; antioxidants; antistatic agents; auxiliary flame retardants, such as antimony trioxide; fillers, such as molybdenum oxide, talc, calcium carbonate, barium sulfate, titanium oxide and inorganic fibers; plasticizers; pigments; crosslinking agents, such as dicumyl peroxide; and so forth. The combined use of an auxiliary flame retardant, such as antimony trioxide, is particularly preferred.

When the production method according to the invention is employed, the imide bond-containing resins of general formula (4) can be obtained in high yields. Furthermore, the imide bond-containing resins of general formula (4) as provided by the invention can provide flammable substances with good fire or flame resistance and at the same time they themselves have remarkable heat resistance and good weather resistance. Therefore, the resins can be used as flame retardants in a broad range of application.

The following examples illustrate the invention in further detail. However, they are by no means limitative of the scope of the invention.

Example 1

A four-necked flask equipped with a stirrer, a cooling condenser, a thermometer and a dropping funnel was charged with 20.2 g of a styrene-maleic anhydride copolymer (comonomer mole ratio = 1:1; average molecular weight = 1,000), 46.4 g of tetrabromophthalic anhydride, 200 g of xylene, 100 g of dimethylformamide, and 1 g of benzyltriphenylphosphonium chloride and the contents were stirred with heating at 80-100 °C. After dissolution of the contents, 16.8 g of hexamethylene diisocyanate was added dropwise to the solution. After completion of the dropping, the flask contents were stirred for 5 hours with heating at 120-135 °C. After the hexamethylene diisocyanate had been consumed, the xylene and dimethylformamide were distilled off under reduced pressure. The remaining reaction product was washed with warm water (80 °C), and then with a mixture of 200 ml of water and 20 g of 28% aqueous ammonia. After collection by filtration, the product was washed with water. After further washing with 200 ml of methanol and collection by filtration, the product was dried. Thus was obtained 70.8 g (yield 95.0%) of an imide bond-containing resin. This resin had a structure such that, in general formula (4), $R_1 = H$, $R_2 = H$, $R_3 = -(CH_2)_6-$, $X = Br$, $l = 1$, $m = 4$, $n = 1$, $p = 1$ and $q = 4.95$.

The elemental analysis and DTA (differential thermal analysis) data obtained with the above resin are shown below.

Elemental analysis:	
Br % :	42.76 (42.89)
C % :	41.86 (41.82)
H % :	2.95 (2.94)
O % :	8.50 (8.58)
N % :	3.71 (3.75)

Hereinabove and hereinafter, the numerical values in the parentheses are calculated values, as far as elemental analysis data are concerned.

DTA analysis:	
10% weight loss :	388 °C
50% weight loss :	471 °C

Example 2

The same reaction apparatus as used in Example 1 was charged with 46.4 g of a bromostyrene-maleic anhydride copolymer (comonomer mole ratio = 2:1; average molecular weight = 2,000), 46.4 g of tetrabromophthalic anhydride, 400 g of xylene and 200 g of dimethylformamide, and the contents were stirred with heating at 80-100 °C. Then, 3 g of ethyltriphenylphosphonium bromide was added thereto, and after dissolution of the contents, 16.8 g of hexamethylene diisocyanate was added dropwise to the solution. After completion of the dropping, the flask contents were stirred for 5 hours with heating at 120-135 °C. The xylene and dimethylformamide were then distilled off from the crystal-containing reaction system under reduced pressure. The remaining reaction product was washed with a mixture of 200 ml of water and 30 g of 28% aqueous ammonia, collected by filtration, and washed with warm water (80 °C). The product was further washed with 400 ml of methanol, collected by filtration, and dried. Thus was obtained 95 g (yield 94.5%) of an imide bond-containing resin. This resin had a structure such that, in general formula (4), $R_1 = H$, $R_2 = Br$, $R_3 = -(CH_2)_6-$, $X = Br$, $l = 1$, $m = 4$, $n = 1$, $p = 2$ and $q = 4.31$.

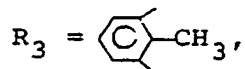
The elemental analysis and DTA analysis data obtained with the above resin are shown below.

Elemental analysis:	
Br % :	47.68 (47.71)
C % :	40.51 (40.55)
H % :	2.55 (2.58)
O % :	6.32 (6.36)
N % :	2.80 (2.78)

DTA analysis:	
10% weight loss :	396 °C
50% weight loss :	-

Example 3

The same apparatus as used in Example 1 was charged with 20.2 g of a styrene-maleic anhydride copolymer (comonomer mole ratio = 1:1; average molecular weight = 3,000), 46.4 g of tetrabromophthalic anhydride, 300 g of xylene and 200 g of dimethylformamide, and the contents were stirred with heating at 80-100 °C. After dissolution of the contents, 5 g of butyltriphenylphosphonium bromide (catalyst) was added and, then, 12.6 g of 2,6-tolylene diisocyanate was added dropwise to the solution. After completion of the dropping, the flask contents were stirred for 6 hours with heating at 120- 140 °C. Thereafter, the reaction product was purified in the same manner as in Example 1. After drying, there was obtained 67.4 g (yield 96.0%) of an imide bond-containing resin. This resin had a structure such that, in general formula (4), $R_1 = H$, $R_2 = H$,



$X = Br$, $l = 1$, $m = 4$, $n = 1$, $p = 1$ and $q = 14.85$.

The elemental analysis and DTA analysis data for the above resin are shown below.

Elemental analysis:	
Br % :	43.40 (42.55)
C % :	42.93 (43.09)
H % :	2.21 (2.13)
O % :	8.42 (8.51)
N % :	3.65 (3.72)

DTA analysis:	
10% weight loss :	398° C
50% weight loss :	-

Example 4

One hundred parts by weight of high impact polystyrene (Nippon Steel Chemical's ESTYRENE® H65) and 15 parts by weight of the imide bond-containing resin obtained in Example 2 were kneaded together on a hot roll mill at 200° C for 5 minutes and then hot-pressed at 210° C for 2 minutes for molding. To determine typical characteristics of the molding, various tests were performed. Results are shown in Table 1. As to the burning test, specimens, 1/16 inch in thickness, were prepared from the molding in accordance with UL 94 (Underwriters Laboratories Inc. Standard for Tests for Flammability of Plastic Materials) and submitted to the test.

Example 5

A mixture of 100 parts by weight of the same high impact polystyrene as used in Example 4, 15 parts by weight of the imide bond-containing resin obtained in Example 2, 2 parts by weight of triphenyl-phosphine oxide and 5 parts by weight of antimony trioxide was kneaded and molded in the same manner as in Example 4. The molding was tested in the same manner as in Example 4. Results are shown in Table 1.

Comparative Examples 1-2

The components shown in Table 1 were kneaded together and molded in the same manner as in Example 4. The molding was tested in the same manner as in Example 4. Results are shown in Table 1.

Table 1

	Example 4	Example 5	Comparative Example 1	Comparative Example 2
High impact polystyrene (parts by weight)	100	100	100	100
Imide bond-containing resin obtained in Example 2 (parts by weight)	15	15	-	-
Decabromodiphenyl oxide (parts by weight)	-	-	13	-
Triphenylphosphine oxide (parts by weight)	-	2	2	-
Antimony trioxide (parts by weight)	-	5	5	-
Impact strength (Izod, notched)*1 (Kgcm/cm)	82	80	64	83
UL94	Classed V-II	Classed V-O	Classed V-O	Burnt
Duration of flaming*2 (seconds)	83.5	5.1	3.9	-
Weather resistance*3 (ΔE)	18	10	46	5

*1: Determined in accordance with JIS K 6871

*2: Duration of burning with flaming combustion

*3: The specimen was irradiated in a Fadeo Meter at 63 ° C for 50 hours and the color difference between the irradiated portion and the unirradiated portion was determined using a color difference meter. A higher value means inferior weather resistance.

Examples 6-7

To a polyamide resin (nylon 6) was added the imide bond-containing resin obtained in Example 3 and the mixture was kneaded and molded in the same manner as in Example 4. The molding was tested for flammability in the same manner as in Example 4. Results are shown in Table 2.

Comparative Example 3

A molding of nylon 6 was tested for flammability in the same manner as in Example 4. Results are shown in Table 2.

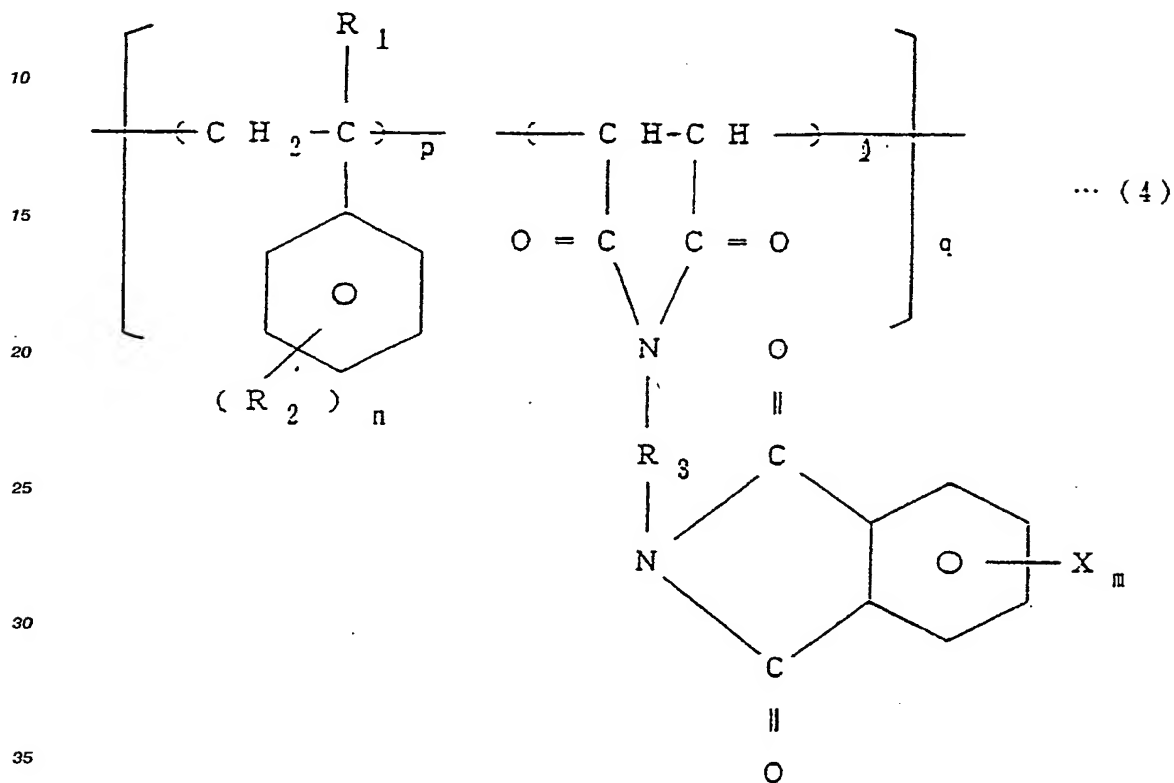
Table 2

	Example 6	Example 7	Comparative Example 3
Nylon 6 (parts by weight)	100	100	100
Imide bond-containing resin obtained in Example 3 (parts by weight)	20	20	-
Antimony trioxide (parts by weight)	-	5	-
UL94	Classed V-II	Classed V-O	Burnt
LOI (Oxygen Index)*	27	29.5	22

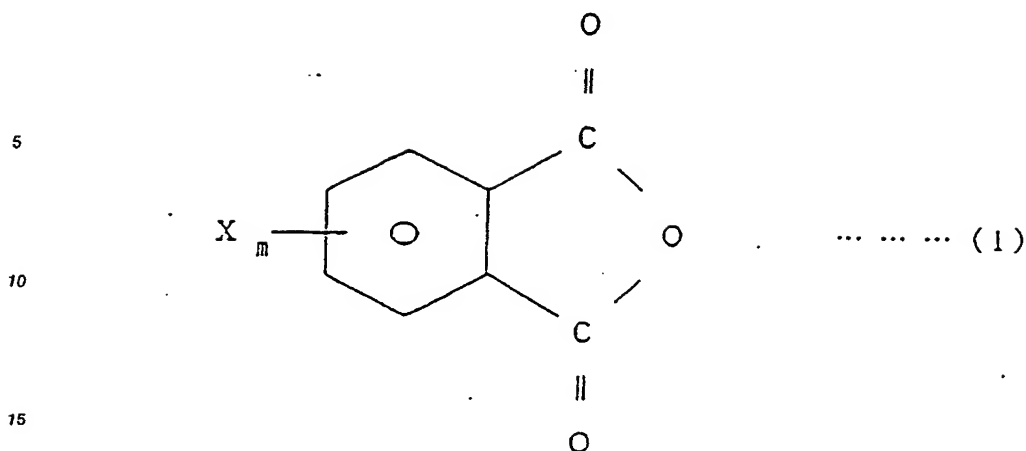
*: Determined in accordance with JIS K 7201

Claims

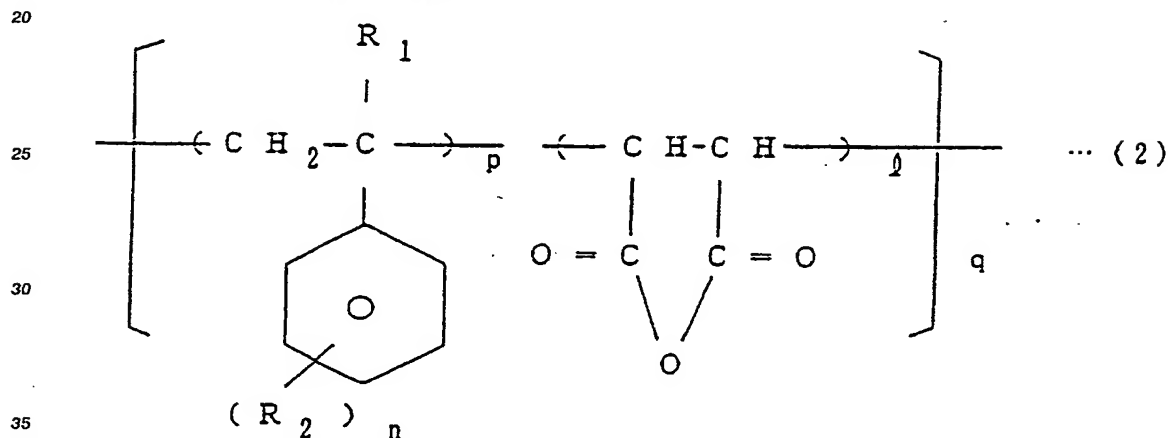
1. A method of producing imide bond-containing resins of the general formula (4)



wherein R_1 is H or CH_3 , R_2 is H, Cl, Br, F or CH_3 , R_3 is an aliphatic, aromatic or alicyclic hydrocarbon group, X is Br, Cl or F, l is equal to 1, m is an integer of 1 to 4, n is an integer of 1 to 5, p is an integer of 1 to 4 and q is a number equal to 1 to 100, which comprises reacting a halogenated phthalic anhydride of the general formula (1)



wherein X and m are as defined above, a copolymer of the general formula (2)



wherein R_1 , R_2 , p , n , t and q are as defined above,
and a diisocyanate compound of the general formula (3)



wherein R_3 is as defined above, in an inert solvent in the presence of a quaternary phosphonium compound as a catalyst.

2. The method of claim 1 wherein said halogenated phthalic anhydride is at least one member selected from the group consisting of tetrachlorophthalic anhydride, tetrabromophthalic anhydride, dichlorophthalic anhydride and dibromophthalic anhydride.

3. The method of claim 1 wherein said copolymer is at least one member selected from the group consisting of a styrene-maleic anhydride copolymer, an α -methylstyrene-maleic anhydride copolymer, a chlorostyrene-maleic anhydride copolymer and a bromostyrene-maleic anhydride copolymer.

4. The method of claim 1 wherein said diisocyanate compound is at least one member selected from the group consisting of 1,6-hexamethylene diisocyanate, diphenylmethane diisocyanate, tolylene diisocyanate, xylene diisocyanate, isophorone diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated tolylene diisocyanate and hydrogenated xylene diisocyanate.

5. The method of claim 1 wherein said quaternary phosphonium compound is at least one member selected from the group consisting of ethyltriphenylphosphonium chloride, benzyltriphenylphosphonium chloride, phenacetyltriphenylphosphonium chloride, acetyltriphenylphosphonium chloride, ethyltriphenylphosphonium bromide, butyltriphenylphosphonium bromide, octyltriphenylphosphonium bromide, 2-methylbenzyltriphenylphosphonium bromide, tetraphenylphosphonium bromide, allyltriphenylphosphonium bromide, benzyltriphenylphosphonium iodide and ethyltriphenylphosphonium iodide.

6. The method of claim 1 wherein said quaternary phosphonium compound is used in an amount of 0.01-10% by weight of the total amount of said halogenated phthalic anhydride plus said copolymer plus said diisocyanate compound.

5 7. The method of claim 1 wherein said inert solvent is at least one member selected from the group consisting of xylene, toluene, dimethylformamide, dimethylacetamide, benzene, cyclohexane and dimethyl sulfoxide.

8. The method of claim 1 wherein said inert solvent is used in an amount of 1 to 10 times the total amount of said halogenated phthalic anhydride plus said copolymer plus said diisocyanate compound.

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